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USAGE OF HIGH-DISPERSION CARBON ADDITIVES INTO ELASTOMER COMPOSITIONS BASED ON RUBBERS OF VARIOUS APPLICATIONS

The effect of carbon nanomaterial (CNM) obtained in high-voltage discharge plasma on properties of elastomeric compositions is investigated. Some tests to determine tensile strength, stretching strain, abrasion resistance, hardness, fatigue endurance and resistance to heat ageing and swelling in aggressive medium of highly filled rubbers based on raw rubber for general and special application are carried out. Parameters of the vulcanization network of the samples are determined by the method of equilibrium swelling. It is shown that CNM addition permits to improve performance characteristics of elastomers based on butadiene-acrylonitrile rubber.

Introduction. At present development of ways of production, investigation of properties and application of various high-dispersion materials is increasingly carried out in order to create highly effective composite materials.

Nanomaterials are particles of 1–100 nm size. High reactivity of similar materials is conditioned by their large specific surface. Because of small size of particles their physicochemical properties are much affected by surface atoms which number is increasing in such conditions.

Methods of nanomaterial production lie in realization of transfers "gas – liquid – solid", "liquid–solid" or "gas – solid" under highly non-equilibrium conditions. This results in the fact that materials composed of high-dispersion particles are characterized by a combination of odd properties and differ from properties of the same materials in bulk. [1–5].

Much attention is paid to development of some directions in the field of investigating new types of materials based on carbon and their application in manufacturing new composite materials. Its morphological states which appear to be of interest for research are diamond films precipitated from the gaseous phase, ultradispersion (ultrafine) particles, nanotubes and fullerenes.

The aim of the research was to determine the effect of carbon nanomaterial (CNM) technical properties of filled rubbers based on raw rubber for general and special application (purpose)

Main part. We investigated filled rubbers based on raw rubber for general application (synthetic-isoprene rubber SKI-3, oil-filled butadiene-styrene rubber SKMS-30 ARKM-15, stereoregular butadiene SKD) and raw rubbers for special application (butadiene-acrylonitrile rubber). Carbon nanomaterials in dosages 0.05–0.20 phr were added into the rubber mix formulations. Samples without nanoadditives in their composition served as the objects for comparison. Codes of the rubbers under analysis are given in Table 1.

The initial nanomaterial was obtained in high-voltage discharge plasma, and after comprehensive treatment with acids and annealing it was divided into fractions. Fractions composed of carbon tubes with some fibre admixtures and amorphous carbon particles were used as additives.

Table 1

Codes of rubbers under analysis

Code of mix	CNM dosage, wt	Raw rubber	Raw rubber content, wt	Fillers	Fillers content, wt
A1	0	SKI-3 SKD SKMS-30 ARKM-15	50 30 20	Carbon black N650	65
A2	0.05				
A3	0.1				
A4	0.15				
A5	0.2				
B1	0	SKI-3 SKMS-30 ARKM-15	73 27	Carbon black N330	53
B2	0.05				
B3	0.1				
B4	0.15				
B5	0.2				
C1	0	SKI-3 SKD	75 25	Carbon black N772 N234 calcium carbonate, zinc oxide	15 15 10 10
C2	0.05				
C3	0.1				
C4	0.15				
C5	0.2				
D1	0	BNKS-18A	100	Carbon black N772	129
D2	0.05				
D3	0.1				
D4	0.15				
D5	0.2				
E1	0	BNKS - 28AM	100	Carbon black N772 N234	95 30
E2	0.05				
E3	0.1				
E4	0.15				
E5	0.2				
F1	0	BNKS - 40AM	100	Carbon black N772	100
F2	0.05				
F3	0.1				
F4	0.15				
F5	0.2				

The carbon nanomaterial was synthesized in the experimental setup (unit) in the laboratory of physics and chemistry of combustion in the Institute of Heat- and Mass Exchange (the National Academy of Sciences of Belarus). The members of the laboratory staff also divided CNM into fractions.

Physico-mechanical characteristics – tensile strength σ_p and breaking elongation ε_p were defined in accordance with State Standard 269-66. Tests to define rubber resistance to heat ageing and aggressive media impact were carried out in accordance with State Standard 9.024-74 (the testing time was 72 hours, the testing temperature of samples based on general-purpose rubbers was 100°C, and based on butadiene-nitrile rubbers – 125°C) and State Standard 9.030-74. Analysis of rubber abrasion resistance was made in accordance with State Standard 426-77. The method of equilibrium swelling [6] was used for defining concentration of cross-links, it helped to calculate such parameters as: ν – cross-linking density and M_c – mean molecular weight of the chain segment between two cross-links.

Discussion of the results. Application of rubber as a construction material is conditioned by its unique ability to deform completely, without damage under low mechanical load, to change its shape at mechanical loading preserving its constant scope, to restore its original shape after removing the load, to absorb the mechanical energy at deforming and diffuse it at restoring

The study of rubber mechanical properties is based on investigation of their physical and chemical structure, nature of highly elastic deformation and relaxation processes. In the majority of cases theoretical knowledge permits to explain peculiarities of mechanical behavior of definite rubbers but it can't be a sufficient basis for creating rubbers with specified mechanical properties [7]. It is accounted for by the fact they are compositions of complex structure and interaction of individual components may occur on molecular and supermolecular levels. So to define the carbon nanomaterial effect on rubber properties we made some tests on revealing dependence of rubber physical and mechanical properties on the rubber type and carbon nanomaterial dosage. The obtained results are presented in Table 2.

The analysis of physical and mechanical properties of vulcanizates revealed that addition of carbon nanomaterials doesn't have much effect on rubber hardness, tensile strength and elongation at break. Perhaps, it is accounted for by a large amount of fillers, including active grades of carbon black. There was observed some decrease of tensile strength in rubbers based on a combination of SKI-3 and SKD. The best combination of properties was displayed by rubbers based on polar BNKS-40AM, addition of CNM leads to some increase in both elastic and strength properties of rubber.

Table 2

Mechanical parameters and their change after thermal agency of rubbers under analysis

Code of mix	Elongation at break, %	Tensile strength, MPa	Change of elongation at break, %	Change of tensile strength, %
A1	700	15.0	–38.7	–45.7
A2	730	14.3	–38.0	–41.2
A3	760	14.6	–36.5	–40.6
A4	750	14.4	–33.4	–42.6
A5	740	13.9	–36.0	–43.0
B1	610	18.9	–25.6	–33.9
B2	600	18.5	–26.5	–31.5
B3	600	18.2	–25.9	–29.6
B4	610	18.3	–25.0	–30.1
B5	620	18.1	–25.8	–30.4
C1	640	22.2	–55.1	–62.2
C2	660	20.7	–55.2	–52.7
C3	660	21.5	–55.6	–54.9
C4	620	19.8	–54.1	–59.1
C5	590	18.1	–53.7	–61.4
D1	220	11.5	–50.0	20.1
D2	210	11.5	–47.0	25.0
D3	210	11.6	–42.3	28.0
D4	210	11.3	–43.2	27.4
D5	200	11.1	–44.0	26.8
E1	260	13.1	–43.0	–11.9
E2	280	12.5	–37.2	–9.7
E3	240	12.7	–38.7	–4.1
E4	250	12.4	–39.3	–4.7
E5	240	12.2	–39.9	–5.0
F1	240	9.9	–49.8	32.0
F2	290	9.7	–45.7	35.0
F3	280	9.8	–44.0	40.2
F4	290	10.0	–43.6	40.6
F5	280	10.3	–43.2	41.0

The data given in Table 2, indicate that carbon nanomaterials in rubber compositions contribute to increase of their thermal stability. The most effective results were obtained in tests on adding carbon nanomaterials into rubber mixes based on butadiene-nitrile raw rubber with acrylonitrile content equal to 17–23% wt. It should be noted that, under the temperature effect on the decrease of elongation at break is slower in rubbers with CNM.

It may be conditioned by the fact that in the process of rubber mix preparation functional groups on the carbon nanomaterial surface can react with raw rubber macromolecules and carbon black surface thus increasing contribution of chemical bonds to interaction of the system "carbon black – elastomeric matrix" [8]. Conditions of rubber service and application should be taken into account in analyzing technical properties of vulcanizates. Thus, rubbers based on a combination of three synthetic raw rubbers (code “A” and “B”) are assigned for tyre manufacture and used for producing parts of sided beads and tyre tread, respectively. Rubbers based on butadiene-nitrile raw rubbers and on a combination of SKI-3 and SKD are used for producing general mechanical rubber goods for various application, which should be sufficiently oil-, petrol- and weather-resistant. Taking into account the service conditions there were carried out some tests on determining rubber resistance to aggressive media and its abrasion resistance, and in case of rubbers for tyre production used for parts of sided bead fatigue endurance seems to be a very important parameter.

The data on rubber abrasion resistance is given in Fig. 1.

The data presented in Fig. 1, indicate that carbon nanomaterial addition results in increase of rubber abrasion resistance. However, the nature of the effect on this parameter depends on the elastomeric matrix. Increase of this parameter value in using polar raw rubbers reaches 25–30% and in case of raw rubber for general (application) purpose it is lower. Thus, the use of CNM in rubber based on a combination of natural and isoprene raw rubbers with stereo-regular butadiene raw rubber allowed to increase their abrasion resistance by 22 and 16% respectively. The rubber samples under test were subjected to abrasive and rolling wear [7]. Increase of abrasion resistance in this case, perhaps, is conditioned (possibly due to) by participation of CNM in the vulcanization process with formation of stronger links. This is vividly seen in increase of Shore A hardness (approximately 5 conv. units. Shore A at increase of carbon nanotube dosage). Increase of rubber hardness in the analyzed types of wear contributes to its decrease [7], since there occurs transition from “rolling” wear to abrasive one.

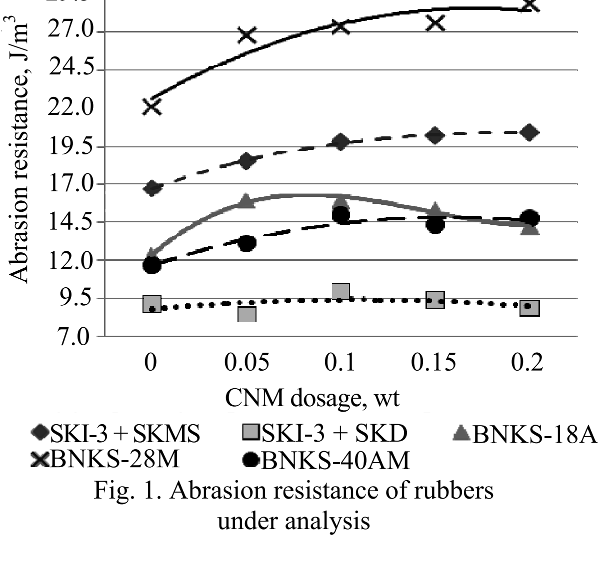

Fig. 1. Abrasion resistance of rubbers under analysis

Rubbers based on a combination of synthetic polyisoprene, stereoregular butadiene and butadiene- styrene rubbers (code “A”), used for producing sided beads must possess high resistance to cyclical loads, these properties are characterized by fatigue endurance and fatigue resistance. Under conditions of constant (stable) strain amplitude the rubber samples containing nanomaterials in dosages 0.10–0.15 phr possess higher resistance to fatigue loads (Fig. 2) which, probably, is connected both with increase of elastomeric composition elasticity and with the fact that carbon nanotubes, to some extent, prevent the occurrence of local overheating and overhead tension in the polymer network [8].

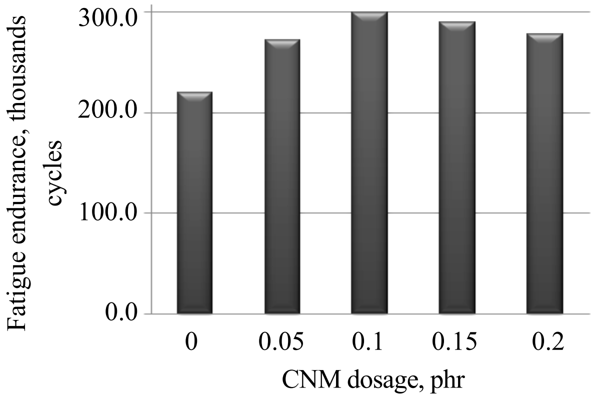

Fig. 2. Fatigue endurance of tyre rubbers of code “A”

The analysis of rubbers based on butadiene-nitrile raw rubber containing acrylonitrile in the dosage 17–23% wt (code “D”), assigned for production of general mechanical rubber goods, proved that nanomaterial additives in the dosage from 0.05 to 0.20 phr lead to increase of vulcanizate resistance to action of hydrocarbon media (Fig. 3).

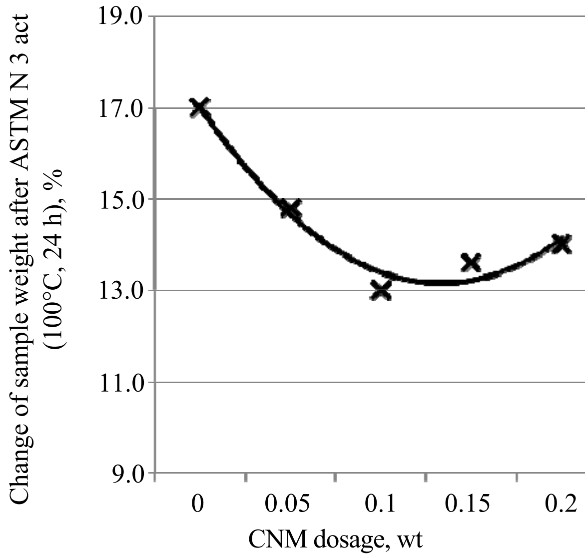

Fig. 3. Rubber (code “D”) resistance to hydrocarbon media action

Increase of rubber resistance to hydrocarbon media action is, perhaps, connected with the fact that nanomaterial, participating in the process of curing, contributs to increase of density of cross-linking [9], which prevents the medium molecules from penetrating into the elastomeric composition structure. This is confirmed by the data (Table 3), obtained in testing the equilibrium swelling of rubber samples (code "D") and calculated by the equation of Flory – Renner [10]:

$$\frac{1}{\mathrm{M_c}} = \frac{V_{r0} + \chi \cdot V_{r0}^2 + \ln(1 - V_{r0})}{\rho_r \cdot V_0 \cdot (V_{r0}^{1/3} - 0{,}5 \cdot V_{r0})},$$

where V_{r0} – volume share of raw rubber in swollen filled vulcanizate; χ – Huggins constant characterizing interaction "polymer – solvent"; ρ_r – density of raw rubber, kg/m^3; V_0 – molar volume of solvent, m^3/mole.

The data, given in Table 3, indicate that addition of carbon nanomaterial results in increase of values of vulcanizate cross-linking density based BNKS-18A by 1.3 times. Increase of density of cross-linking is, probably, connected with a more complete procedure of the vulcanization reaction which is a consequence of the interaction of the CNM particles with the vulcanizing system of elastomeric compositions.

Table 3

Characteristics of vulcanization network of rubber (code "D") samples

Code of mix	$\nu \cdot 10^4$, mole/cm^3	$\mathrm{M_c}$, g/mole	$n \cdot 10^{-19}$, cm^{-3}
D1	1.22	7,750	7.34
D2	1.44	6,570	8.66
D3	1.57	6,050	9.44
D4	1.48	6,410	8.88
D5	1.37	6,890	8.26

Note: ν – density of cross-linking, mole/cm^3; $\mathrm{M_c}$ – mean molecular weight of chain segment between two cross-links, g/mole; n – concentration of cross-links, cm^{-3}.

Conclusion. Addition of carbon nanomaterials into rubber formulations based on general-purpose rubbers should be carried out with the account of the formulation, nature of polymer and service characteristics. In this case, as our investigation showed, there occurs increase of certain properties of rubbers. Thus, it is most reasonable to create new elastomer compounds with the use of CNM as modifying additives on the basis of butadiene-nitrile raw rubbers. Vulcanizates of such structure are characterized by high abrasion resistance, resistance to heat ageing and liquid aggressive media action.

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